

Heats of Transformations in Bismuth Oxide by Differential Thermal Analysis

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DTA was chosen as a convenient method for resolving differences in the reported heat of transition and heat of fusion of Bi_2O_3 . The heat of the low to high transition of K_2SO_4 (at 583 °C) and the heat of fusion of Ag (at 960.8 °C) were used as internal standards. These standards were mixed directly with the Bi_2O_3 in three weight ratios. The heating schedule for each weight ratio was 3°/min, 9°/min, and 3°/min. For evaluating internal consistency, DTA determinations were made for mixtures of the two standards. Linearity was obtained within limits between the weight ratio of Bi_2O_3 and standard and the corresponding ratio of peak areas. The heat of transition of Bi_2O_3 (mon $\xrightarrow{730^\circ\text{C}}$ cubic was found to be 9.9 ± 0.5 kcal/mole and the heat of fusion (cubic $\xrightarrow{825^\circ\text{C}}$ liq.) 3.9 ± 0.2 kcal/mole. The uncertainties are estimated limits of error, based on internal consistency and on the values of the standards.

1. Introduction

By application of the Clausius-Clapeyron equation to the liquidus curve of the Bi_2O_3 -PbO system [1],¹ K. K. Kelley determined the heat of fusion of Bi_2O_3 to be 6.8 kcal/mole [2]. This value is listed in tables of thermodynamic data [3, 4]. Levin and McDaniel [5] applying the same Clausius-Clapeyron equation to the Bi_2O_3 - B_2O_3 system obtained a heat of fusion value of 2.0₅ kcal/mole. Gattow and Schröder [6] and Gattow and Schütze [7] have used these two values in conjunction with differential thermal analysis (DTA) data to calculate the heat of transition of monoclinic- to cubic-bismuth oxide (see table 1). They found that the area of the peak representing the monoclinic to cubic transition was 4.10 ± 0.11 times the area of the peak representing the cubic to liquid transformation; and, consequently, the heat of transition should be 4.10 \times the heat of fusion.

The two reported values for the heat of fusion of Bi_2O_3 differ by a factor of about three. The value of 6.8 kcal/mole obtained from the Bi_2O_3 -PbO diagram is suspect for two reasons: First, a reinvestigation of the Bi_2O_3 -PbO system [8] has shown Belladen's simple liquidus diagram to be incorrect, inasmuch as PbO exists in solid solution with Bi_2O_3 at the liquidus. Second, the sum of the reported entropy of transition and of fusion, $\left(\frac{6800}{1098} + \frac{27900}{1003}\right)/5$, is about 7 cal/°K/g atom, an abnormally high value.

Because of the increasing importance of Bi_2O_3 in the electronics and ceramics industries, it is desirable to verify the basic thermodynamic data. As equipment for direct calorimetric measurement was not available, differential thermal analysis, using internal standards, was selected as a convenient, independent method for determining heats of transformation.

2. Equipment

The differential thermal analysis equipment was built in the laboratory and is of conventional design. The furnace heating element consists of a ceramic core 10 in. long \times 2 $\frac{3}{8}$ in. o.d., wound with 20 gage, 80 percent Pt: 20 percent Rh, wire. Linear temperature rise with time is accomplished by means of a program controller and a pneumatically activated variable auto-transformer. Heating rates of 3°/min and 9°/min are obtained by controlling the percentage of time during which the set point is driven. Using a multipoint recorder, the emfs of the sample thermocouple and of the differential thermocouple are plotted as a function of time. Determinations are made at overall sensitivities of 14 $\mu\text{V/in.}$

To minimize errors that might be caused by poor thermal diffusivity, a special holder assembly is used.

TABLE 1. *Heats of transformations in bismuth oxide*

Investigator	Method	Heat of transformation	
		Transition (mon \rightarrow c)	Fusion (c \rightarrow liq)
K. K. Kelley (1936) [2]	Bi_2O_3 -PbO liquidus [1]	kcal/mole	kcal/mole
Levin and McDaniel (1962) [5]	Bi_2O_3 - B_2O_3 liquidus		6.8
Gattow and Schröder (1962) [6]	DTA ^a	27.9 ± 1.0	2.0 ₅
Gattow and Schütze (1964) [7]	DTA ^b	8.4 ± 0.3	
Levin and McDaniel (1964)	DTA ^c	9.9 ± 0.5	3.9 ± 0.2

^a Heat of transformation = $(4.10 \pm 0.11) \times$ heat of fusion (6.8 kcal/mole).

^b Heat of transformation = $(4.10 \pm 0.11) \times$ heat of fusion (2.0₅ kcal/mole).

^c Using K_2SO_4 and Ag as internal standards.

¹ Figures in brackets indicate the literature references at the end of this paper.

The two thermocouples (Pt—90 percent Pt:10 percent Rh) from the holder assembly are welded, near the bottom, to Pt containers. The containers are made from Pt tubing and measured 16 mm long \times 2.6 mm i.d. \times 3.0 mm o.d. The tubes contain a total of 0.2 to 0.4 g of material, depending on the substances and weight ratios studied. To reduce the effect of air currents in the furnace, the Pt tubes are covered with thin ceramic thimbles.

3. Method

The usual procedure for measuring heats of transformation by DTA depends on calibration of the equipment with a known weight of a standard, e.g., benzoic acid, AgNO_3 , KNO_3 [9, p. 111] and [10, 11]. The calibration can be expressed in terms of calories per unit of integrated peak area, in the differential temp.-time curve representing the transformation. Assuming approximate constancy of the calibration factor, the unknown heat of transformation for a substance can be determined from the peak area in its differential temp.-time curve.

The method depends on conditions that are seldom closely realized. First, the geometry of the physical arrangement and other operating conditions should be exactly the same for the determination of the unknown as for the calibration with the standard. Second, and even more unlikely, such thermal properties as conductivity, diffusivity, and specific heat should be essentially identical for the two samples.

A method using internal standards avoids the problems inherent in a separate calibration method. Therefore, several high-purity chemicals, with appropriate temperatures and heats of transformations were tried, in a search for internal standards.

Two substances were found satisfactory for calibrants: (1) Finely ground crystalline K_2SO_4 with a heat of transition ($\alpha^{583} \rightarrow \beta$) of 2.14 kcal/mole [3, 12]. (2) Fine, precipitated Ag powder with a heat of fusion ($s^{960.8} \rightarrow \text{liq.}$) of 2.61 kcal/mole² [13]. The transformation temperatures in these two substances bracket the transition temp. of Bi_2O_3 (monoclinic $^{730} \rightarrow$ cubic) and the fusion temp. of Bi_2O_3 (cubic $^{825} \rightarrow$ liquid). Two additional substances, NaCl and Li_2SO_4 , were found to be unsatisfactory as internal calibration standards.

DTA experiments were carried out for Bi_2O_3 : K_2SO_4 mixtures in wt. ratios of 3.46:1, 1.72:1, and 1.00:1; and for Bi_2O_3 :Ag mixtures in wt ratios of 4.32:1, 2.16:1, and 2.00:1. Mixtures were in 2g batches by shaking in a mechanical mixer accurately weighed amounts of dried starting materials. As will be shown below under "Derivation of Equations" the heat of transformation calculations are not based on the actual weights of the two substances in the sample holder but only on the formulated ratios.

Each mixture was given a preliminary heat-cycling treatment by heating the mixture at 12 $^\circ\text{C}/\text{min}$ to about

775 $^\circ\text{C}$ (above the transition of K_2SO_4 and Bi_2O_3 but below the melting point of Bi_2O_3) and then cooling to room temperature. The preliminary heat treatment was followed by three successive cycles of heating to above the mp of Bi_2O_3 in K_2SO_4 mixtures and above the mp of Ag in Ag mixtures. The heating and cooling rates for the three cycles were 3 $^\circ/\text{min}$, 9 $^\circ/\text{min}$, and 3 $^\circ/\text{min}$, respectively. Only the peak areas in heating curves were considered, as previous work, using both DTA and high-temperature x-ray techniques [14], had shown that the stable high-temperature cubic phase is supercooled below the equilibrium transition temperature of 730 $^\circ\text{C}$; and at about 650 $^\circ\text{C}$ a metastable tetragonal and/or body-centered cubic phase is formed, which in turn, transforms back to the stable monoclinic form.

To check on the internal consistency of the method and to evaluate the accuracy, DTA determinations were made with mixtures of the two standards, at the same heating rates and at weight ratios of K_2SO_4 :Ag of 1.36:1 and 4.00:1.

It should be noted that a number of investigators [9] have used internal standards for quantitative estimation of a phase. Barshad [11] has proposed using "indicators" either mixed with the sample or in separate layers, for direct temperature calibration of a DTA curve. However, the use of internal standards for heat of reaction measurements as herein proposed has not been previously reported, according to the best knowledge of the authors.

An obvious and valid *a priori* criticism of the internal-standard method is the possibility of obtaining erroneous results if reaction occurs between the bismuth oxide and the standards during the heat-cycling treatments. This possibility was foreseen and was shown to be minimal by a number of observations.

(1) The ratio of the areas under the peaks representing the monoclinic to cubic transition and the cubic to liquid transformation for pure Bi_2O_3 could be compared with the corresponding ratio when standards were mixed with the Bi_2O_3 .

(2) Ratios of corresponding areas for successive heat cycles could be compared with each other, and any discrepancies noted.

(3) At the conclusion of each series of determinations for a given weight ratio, the mixture was examined by x-ray powder diffraction techniques to check for any new phases that might have formed by reaction of the starting materials.

(4) Finally, experimental results could be checked for conformance to theory.

By the criteria listed above, it was possible to evaluate the individual experimental data and to eliminate the few values which were obviously in error. However, even in these instances, the evidence did not indicate chemical reaction of the Bi_2O_3 , but pointed to physical factors.

4. Derivation of Equations

It can be shown that to a close approximation [9, p. 111] the total heat of reaction in a DTA determination

²The literature values reported for the heats of transformations in K_2SO_4 and Ag vary over a range of about 10 percent. The values selected here are shown later in this paper (see Internal Consistency) to be self-consistent.

is given by:

$$\Delta H = \frac{cK_s}{g} \int ydt = \frac{cK_s}{g} \cdot A \quad (1)$$

where, H = heat of transformation per g

c = geometrical shape constant

K_s = thermal conductivity of the sample

g = mass of reactive component in sample

$$\int ydt = A = \text{peak area for the transformation.}$$

If two substances, designated by subscripts 1 and 2, are considered in a mixture, eq (1) may be applied to each substance. Assuming no reaction between the substances, constancy in c , and approximate constancy in K_s (now the combined thermal conductivity of the mixture), the following expression is readily obtained:

$$\frac{\Delta H_1}{\Delta H_2} = \frac{A_1 g_2}{A_2 g_1} \quad (2)$$

As ΔH_1 and ΔH_2 are constants, g_2/g_1 is the weight ratio of the binary mixture, as formulated, and A_1/A_2 is the experimentally measured peak area ratio of the two transformations, the basic equation for an unknown heat of transformation becomes:

$$\Delta H_1 = \Delta H_2 \left(\frac{g_2}{g_1} \right) \left(\frac{A_1}{A_2} \right) \quad (3)$$

It may be noted that eq (3) is a straight line that passes through the origin and with slope, m , equal to $(A_1/A_2)/(g_1/g_2)$. Thus, over the range that the assumptions made in the derivation hold true, a linear relationship should exist between the formulated weight ratios and the corresponding measured peak area ratios.

If the heat of transformation is desired directly in kcal/mole rather than on a gram basis, eq (3) may be transformed to:

$$L_1 = L_2 \left(\frac{M_1}{M_2} \right) \left(\frac{A_1}{A_2} \right) \left(\frac{g_1}{g_2} \right) \quad (4)$$

where, L_1 and L_2 are the heats of transformation of substances 1 and 2, respectively, in kcal/mole, and

M_1 and M_2 are the corresponding molecular weights.

Applying eq (4) to the specific case of Bi_2O_3 : K_2SO_4 mixtures:

$$L_{\text{Bi}_2\text{O}_3} = 2.14 \left(\frac{465.96}{174.27} \right) \left(\frac{A_{\text{Bi}_2\text{O}_3}}{A_{\text{K}_2\text{SO}_4}} \right) \left(\frac{g_{\text{Bi}_2\text{O}_3}}{g_{\text{K}_2\text{SO}_4}} \right) = 5.722m_1 \quad (5)$$

where, $L_{\text{Bi}_2\text{O}_3}$ refers to the heat of transformation (transition or fusion), in kcal/mole;

2.14 = the heat of transition of K_2SO_4 , from the α to β form, in kcal/mole;

465.96/174.27 = the molecular weight ratio of Bi_2O_3 to K_2SO_4 ; and

m_1 = the slope of the line obtained by plotting as ordinate the ratio of the peak areas representing the particular transformation of Bi_2O_3 to the transition of K_2SO_4 ($A_{\text{Bi}_2\text{O}_3}/A_{\text{K}_2\text{SO}_4}$) and plotting as abscissa the corresponding weight ratio of Bi_2O_3 to K_2SO_4 ($g_{\text{Bi}_2\text{O}_3}/g_{\text{K}_2\text{SO}_4}$).

Applying eq (4) to the case of Bi_2O_3 : Ag mixtures:

$$L_{\text{Bi}_2\text{O}_3} = 2.61 \left(\frac{465.96}{107.87} \right) \left(\frac{A_{\text{Bi}_2\text{O}_3}}{A_{\text{Ag}}} \right) \left(\frac{g_{\text{Bi}_2\text{O}_3}}{g_{\text{Ag}}} \right) = 11.274m_2 \quad (6)$$

where, 2.61 = the heat of fusion of Ag, in kcal/mole, 465.96/107.87 = the molecular weight ratio of Bi_2O_3 to K_2SO_4 , and m_2 is the slope of the line

obtained by plotting $\frac{A_{\text{Bi}_2\text{O}_3}}{A_{\text{Ag}}}$ as ordinate versus $\frac{g_{\text{Bi}_2\text{O}_3}}{g_{\text{Ag}}}$ as abscissa.

Applying eq (4) to the case of mixtures of the two standards, K_2SO_4 and Ag:

$$L_{\text{K}_2\text{SO}_4} = 2.61 \left(\frac{174.27}{107.87} \right) \left(\frac{A_{\text{K}_2\text{SO}_4}}{A_{\text{Ag}}} \right) \left(\frac{g_{\text{K}_2\text{SO}_4}}{g_{\text{Ag}}} \right) = 4.217m_3 \quad (7)$$

where, $L_{\text{K}_2\text{SO}_4}$ = the heat of transition of K_2SO_4 , in kcal/mole;

2.61 = the heat of fusion of Ag, in kcal/mole 174.27/107.87 = the molecular weight ratio of K_2SO_4 to Ag; and

m_3 = the slope of the line obtained by plotting $\frac{A_{\text{K}_2\text{SO}_4}}{A_{\text{Ag}}}$ as ordinate versus $\frac{g_{\text{K}_2\text{SO}_4}}{g_{\text{Ag}}}$ as abscissa.

Inasmuch as DTA determinations were made in binary combinations of the three substances, Bi_2O_3 , K_2SO_4 , and Ag, it is possible to evaluate the internal consistency of the method. From eqs (5), (6), and (7), where m_1 , m_2 , and m_3 are given in terms of the specific ratios, it follows that any one ratio can be determined independently from the other two, for example:

$$\frac{A_{\text{Bi}_2\text{O}_3}}{A_{\text{Ag}}} \cdot \frac{g_{\text{Ag}}}{g_{\text{Bi}_2\text{O}_3}} = \frac{A_{\text{K}_2\text{SO}_4}}{A_{\text{Ag}}} \cdot \frac{g_{\text{Ag}}}{g_{\text{K}_2\text{SO}_4}} \quad (8)$$

$$\frac{A_{\text{Bi}_2\text{O}_3}}{A_{\text{K}_2\text{SO}_4}} \cdot \frac{g_{\text{K}_2\text{SO}_4}}{g_{\text{Bi}_2\text{O}_3}} \quad (9)$$

or $m_2/m_1 = m_3$.

5. Results and Discussion

5.1. General

Figure 1 shows a reproduction of the DTA curve for one of the $\text{Bi}_2\text{O}_3:\text{K}_2\text{SO}_4$ mixtures. The various transformations within the phases are labeled. Peak areas were obtained by tracing the curve on millimeter ruled graph paper and averaging several counts. The modification of the sample holder in conjunction with the amplification of the equipment was found to be sensitive to heat of reaction effects. In a 1:1 mixture of $\text{Bi}_2\text{O}_3:\text{K}_2\text{SO}_4$, for example, 0.1192 g K_2SO_4 absorbed a calculated 1.4635 calories of heat at the transition and produced an area under the peak of 208 mm^2 , or about 0.007 cal/ mm^2 . No corrections were applied to the area data for change in thermocouple (Pt-90 percent Pt:10 percent Rh) sensitivity with temperature. Attempted corrections did not improve the results; furthermore, the use of two standards whose transformation temperatures bracketed those of Bi_2O_3 provided automatic compensation.

The experimentally determined transformation ratios for pure Bi_2O_3 and the binary mixtures between Bi_2O_3 , K_2SO_4 , and Ag are given in table 2. Transformation ratios as a function of weight ratios are plotted in figures 2, 3, and 4. Slopes of the lines and standard deviations of the slopes were determined by the method of least squares for lines passing through the origin. If the assumptions used previously in deriving the linear relationships hold, then the origin

constitutes a valid fixed point, for obviously as $g_{\text{Bi}_2\text{O}_3}$ in the mixture approaches 0, so does $A_{\text{Bi}_2\text{O}_3}$ and consequently so do the ratios $g_{\text{Bi}_2\text{O}_3}/g_{\text{K}_2\text{SO}_4}$ and $A_{\text{Bi}_2\text{O}_3}/A_{\text{K}_2\text{SO}_4}$.

Examining the transformation ratios (table 2) as a function of the 3°/min and 9°/min heating rates or as a function of the heating cycle (1st, 2d, or 3d), no overall trend of statistical significance can be discerned. The average ratios of the Bi_2O_3 transformations ($M \rightarrow c/c \rightarrow l$) of 2.54 and 2.52 for the $\text{Bi}_2\text{O}_3:\text{K}_2\text{SO}_4$ mixtures and of 2.53 for the $\text{Bi}_2\text{O}_3:\text{Ag}$ mixture (4.32:1) are in good agreement with each other and with that for pure Bi_2O_3 , 2.46. However, the ratios of 3.20 and 2.80 for the Bi_2O_3 transformations in the Ag mixtures (2.16:1 and 2.00:1) appear high. The heat of fusion of Bi_2O_3 is 2/5 that of the heat of transition, and the shape of the fusion peak tends to be low and flat (see fig. 1). Therefore, as the amount of Bi_2O_3 decreases in the mixture, the peak area for fusion becomes less defined and broader tending to give a low area count.

It may be noted in figure 2 for the $\text{Bi}_2\text{O}_3:\text{K}_2\text{SO}_4$ mixtures that the curves deviate from linearity above a 2:1 wt ratio of $\text{Bi}_2\text{O}_3:\text{K}_2\text{SO}_4$. This deviation is not due to any significant reaction between Bi_2O_3 and K_2SO_4 but to poor thermal properties of the Bi_2O_3 mixture. For the mixtures containing Ag, which is a good thermal conductor and which has been used to improve thermal transfer [9, 15], linearity extends beyond the 4:1 ratio of substance to Ag (fig. 3 and 4). Therefore, the area ratios for the 3.46 to 1 wt ratio of Bi_2O_3 to K_2SO_4 were not used in computing the slopes.

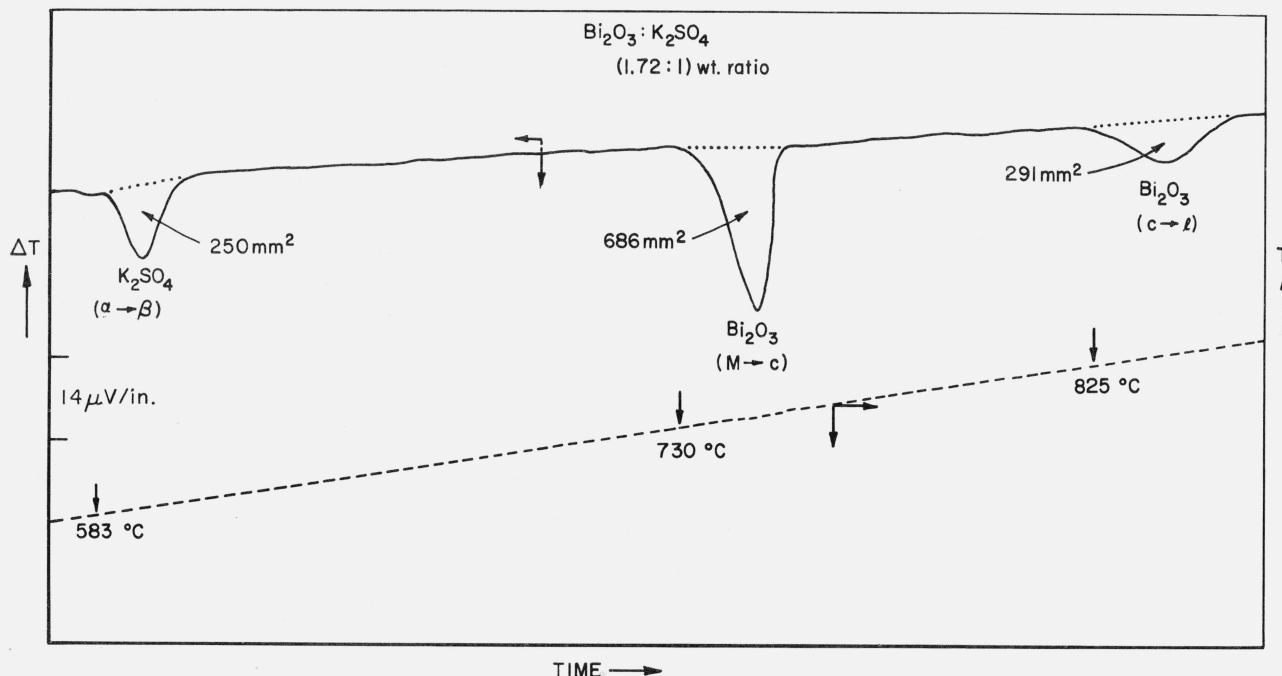


FIGURE 1. Differential thermal analysis curve for third cycle of heat treatment of $\text{Bi}_2\text{O}_3:\text{K}_2\text{SO}_4$ mixtures of weight ratio 1.72:1.

Approx. 0.2 g of sample in Pt tube was heated in air at 3°/min. The temperature of sample container was measured with Pt-90 percent Pt:10 percent Rh thermocouple; reference material was compacted alumina powder. Areas under peaks were obtained by counting squares in tracings of the peaks on millimeter ruled graph paper.

$\alpha \rightarrow \beta$ = transition of K_2SO_4
 $M \rightarrow c$ = monoclinic to cubic transition of Bi_2O_3
 $c \rightarrow l$ = fusion of cubic Bi_2O_3 .

TABLE 2. Ratio of peak areas between transformations in Bi_2O_3 and in binary mixtures of Bi_2O_3 , K_2SO_4 , and Ag, as a function of heating rates and weight ratios*

Composition wt. ratio	Transformation ratios ^a A_1/A_2	Ratio of peak areas at heating rates:			
		3°/min	9°/min	3°/min	Average
Bi ₂ O ₃ (pure)					
	$\frac{M \rightarrow c}{c \rightarrow l}$	2.47	2.57	2.33	2.46
Bi ₂ O ₃ : K ₂ SO ₄ mixtures					
77.6 Bi ₂ O ₃ 22.4 K ₂ SO ₄ (3.46 : 1)	$\frac{M \rightarrow c}{c \rightarrow l}$	2.86	2.18	2.58	2.54
	$\frac{M \rightarrow c}{\alpha \rightarrow \beta}$	4.67	4.87	4.57	4.70
	$\frac{c \rightarrow l}{\alpha \rightarrow \beta}$	1.63	2.23	1.92	1.93
63.3 Bi ₂ O ₃ 36.7 K ₂ SO ₄ (1.72 : 1)	$\frac{M \rightarrow c}{c \rightarrow l}$	2.51	2.70	2.36	2.52
	$\frac{M \rightarrow c}{\alpha \rightarrow \beta}$	3.03	2.94	2.74	2.90
	$\frac{c \rightarrow l}{\alpha \rightarrow \beta}$	1.21	1.09	1.16	1.15
50.0 Bi ₂ O ₃ 50.0 K ₂ SO ₄ (1.00 : 1)	$\frac{M \rightarrow c}{\alpha \rightarrow \beta}$ ^b	1.61	1.61	1.62	1.61
Bi ₂ O ₃ : Ag mixtures					
81.2 Bi ₂ O ₃ 18.8 Ag (4.32 : 1)	$\frac{M \rightarrow c}{c \rightarrow l}$	2.56	2.52	2.51	2.53
	$\frac{M \rightarrow c}{s \rightarrow l}$	3.91	3.82	3.96	3.90
	$\frac{c \rightarrow l}{s \rightarrow l}$	1.52	1.51	1.58	1.54
68.35 Bi ₂ O ₃ 31.65 Ag (2.16 : 1)	$\frac{M \rightarrow c}{c \rightarrow l}$	3.10 ^{c, d}	3.29 ^d	3.20 ^d
	$\frac{M \rightarrow c}{s \rightarrow l}$	2.14 ^c	1.68	1.91
	$\frac{c \rightarrow l}{s \rightarrow l}$	0.69 ^c	0.51	0.60
66.7 Bi ₂ O ₃ 33.3 Ag (2.00 : 1)	$\frac{M \rightarrow c}{c \rightarrow l}$	2.80	2.80 ^d
	$\frac{M \rightarrow c}{s \rightarrow l}$	1.99	1.72	1.86
	$\frac{c \rightarrow l}{s \rightarrow l}$	0.61	0.61
K ₂ SO ₄ : Ag mixtures					
57.7 K ₂ SO ₄ 42.3 Ag (1.36 : 1)	$\frac{\alpha \rightarrow \beta}{s \rightarrow l}$	0.637	0.638	0.604	0.626
80.0 K ₂ SO ₄ 20.0 Ag (4.00 : 1)	$\frac{\alpha \rightarrow \beta}{s \rightarrow l}$	2.27	2.16	2.07	2.17

* Sample weights varied from 0.2 to 0.4 g, depending on the particular mixtures. Samples were contained in Pt tubes and heated in air. Sensitivity on the differential temperature scale was 14 $\mu\text{V}/\text{in}$.

^a Refers to ratio of peak areas between the indicated transformations:

$M \rightarrow c$, monoclinic to cubic transition of Bi_2O_3 phase at 730 °C

$c \rightarrow l$, cubic to liquid transformation of Bi_2O_3 phase at 825 °C

$\alpha \rightarrow \beta$, low to high transition of K_2SO_4 phase at 583 °C

$s \rightarrow l$, solid to liquid transformation of Ag phase at 960.8 °C.

^b No values for $\frac{M \rightarrow c}{c \rightarrow l}$ and $\frac{c \rightarrow l}{\alpha \rightarrow \beta}$ ratios as $c \rightarrow l$ transformation of Bi_2O_3 is not well defined.

^c 12°/min heating rate.

^d Area for $c \rightarrow l$ transformation of Bi_2O_3 appears low.

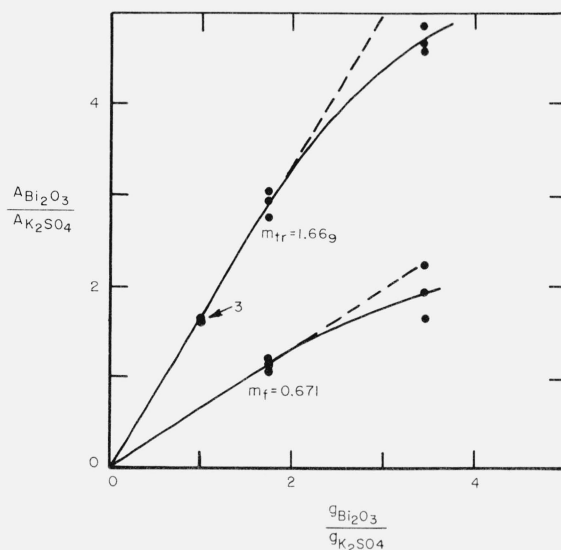


FIGURE 2. Peak area ratios versus weight ratios for mixtures of Bi_2O_3 and K_2SO_4 .

$g_{\text{Bi}_2\text{O}_3}/g_{\text{K}_2\text{SO}_4}$ refers to the weight ratio. $A_{\text{Bi}_2\text{O}_3}/A_{\text{K}_2\text{SO}_4}$ for slope of line m_{tr} refers to area under transition of $\text{Bi}_2\text{O}_3 \div$ area under transition of K_2SO_4 . $A_{\text{Bi}_2\text{O}_3}/A_{\text{K}_2\text{SO}_4}$ for slope of line m_f refers to area under fusion of $\text{Bi}_2\text{O}_3 \div$ area under fusion of K_2SO_4 . Slopes calculated by method of least squares.

$L_{\text{Bi}_2\text{O}_3} = 5.722 m_1$ (see eq (5), in text).

$L_{tr}\text{Bi}_2\text{O}_3 = 5.722 \times 1.669 = 9.5$ kcal/mole. S.D. $m_{tr} = 0.031$.

$L_f\text{Bi}_2\text{O}_3 = 5.722 \times 0.671 = 3.8$ kcal/mole. S.D. $m_f = 0.020$.

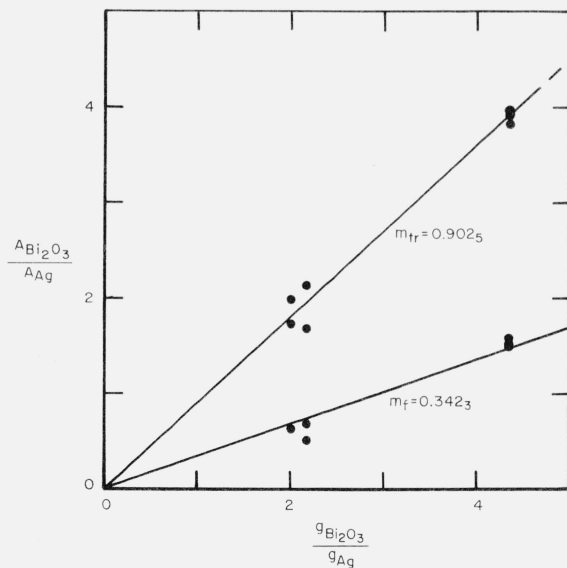


FIGURE 3. Peak area ratios versus weight ratios for mixtures of Bi_2O_3 and Ag.

$g_{\text{Bi}_2\text{O}_3}/g_{\text{Ag}}$ refers to the weight ratio. $A_{\text{Bi}_2\text{O}_3}/A_{\text{Ag}}$ for slope of line m_{tr} refers to area under transition of $\text{Bi}_2\text{O}_3 \div$ area under fusion of Ag. $A_{\text{Bi}_2\text{O}_3}/A_{\text{Ag}}$ for slope of line m_f refers to area under fusion of $\text{Bi}_2\text{O}_3 \div$ area under fusion of Ag. Slopes calculated by method of least squares.

$L_{\text{Bi}_2\text{O}_3} = 11.274 m_2$ (see eq (6), in text).

$L_{tr}\text{Bi}_2\text{O}_3 = 11.274 \times 0.9025 = 10.1$ kcal/mole. S.D. $m_{tr} = 0.019$.

$L_f\text{Bi}_2\text{O}_3 = 11.27 \times 0.3423 = 3.8$ kcal/mole. S.D. $m_f = 0.015$.

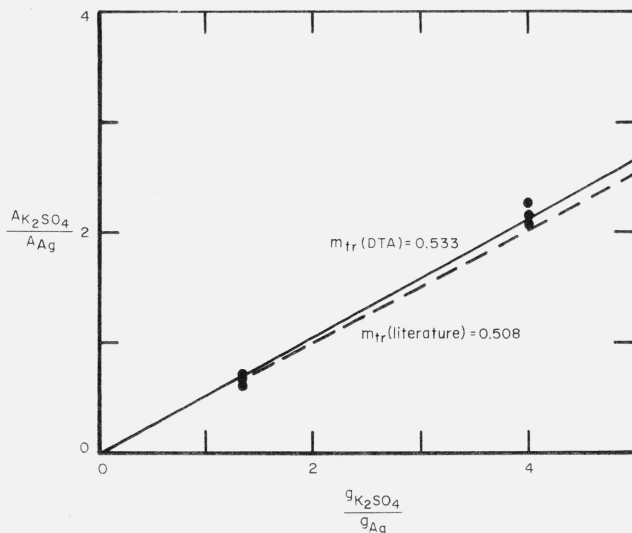


FIGURE 4. Peak area ratios versus weight ratios for mixtures of K_2SO_4 and Ag.

$g_{K_2SO_4}/g_{Ag}$ refers to the weight ratio. $A_{K_2SO_4}/A_{Ag}$ for slope of line m_{tr} (DTA) refers to the area under the transition of K_2SO_4 ÷ area under the fusion of Ag. Slope for solid line calculated by method of least squares; slope for dashed line calculated from literature values. $L_{K_2SO_4} = 4.217 m_3$ (see eq (7), in text). $L_{tr}K_2SO_4 = 4.217 \times 0.533 = 2.25$ kcal/mole. S.D. $m_{tr} = 0.014$. $L_{tr}K_2SO_4$, from literature [3, 12] = 2.14 kcal/mole.

5.2. Heats of Transformations

By application of eq (5) to the slopes in figure 2:

$$L_{tr}Bi_2O_3(M \rightarrow c) = 5.722 \times 1.669 = 9.55 \text{ kcal/mole}$$

$$\text{S.D. } m_{tr} = 0.031 \text{ (0.30 kcal/mole)}$$

$$L_fBi_2O_3(c \rightarrow l) = 5.722 \times 0.671 = 3.84 \text{ kcal/mole}$$

$$\text{S.D. } m_f = 0.020 \text{ (0.08 kcal/mole)}$$

Similarly, by application of eq (6) to the slopes for the Bi_2O_3 :Ag mixtures (fig. 3):

$$L_{tr}Bi_2O_3(M \rightarrow c) = 11.274 \times 0.9025 = 10.17 \text{ kcal/mole}$$

$$\text{S.D. } m_{tr} = 0.019 \text{ (0.19 kcal/mole)}$$

$$L_fBi_2O_3(c \rightarrow l) = 11.274 \times 0.3423 = 3.86 \text{ kcal/mole}$$

$$\text{S.D. } m_f = 0.015 \text{ (0.06 kcal/mole)}.$$

The standard deviations of the slopes for the Bi_2O_3 :Ag mixtures are somewhat lower than for the Bi_2O_3 : K_2SO_4 mixtures because of the additional data, for the high weight ratio, that could be used in the calculations. Certainly, the difference in the heat of fusion of Bi_2O_3 obtained from the two standards is not statistically significant. The difference in values for the heat of transition is of questionable significance.

5.3. Accuracy

The linear relationship between area ratios and weight ratios for mixtures of the two standards can be seen in figure 4. The experimentally determined slope (0.533) is 4.7 percent greater than the theoretical slope (0.508) derived from the literature values. The difference between slopes is about twice the standard deviation of the experimentally determined slope. The agreement is good considering that the binary mixture of standards presents the most extreme in physical conditions of the three binary mixtures. In the K_2SO_4 :Ag mixtures, the area of the solid-solid transition of K_2SO_4 at 583 °C is compared to the area of the solid-liquid transformation of Ag at 960.8 °C.

Substituting in eq (7) the slope of the transformation ratio shown in figure 4 (0.533) gives a value of 2.25 kcal/mole for the heat of transition of K_2SO_4 , compared to 2.14, the literature value. The agreement between these two values, as well as for the slopes, tends to substantiate the standard values used in the calculations, namely, 2.61 kcal/mole for L_f of Ag and 2.14 kcal/mole for L_{tr} of K_2SO_4 . Attempts to correct for the change in thermocouple sensitivity with temperature or the use of other literature values for the heats of transformation of the standards has a detrimental effect on the agreement.

5.4. Internal Consistency

As shown in the development of eqs (8) and (9), it is possible to check the internal consistency of the results through a calculation which does not involve any heat of transformation values. From eqs (8) and (9):

$$\frac{m_2}{m_1} = m_3 = \frac{A_{K_2SO_4}}{A_{Ag}} \cdot \frac{g_{Ag}}{g_{K_2SO_4}}.$$

Substituting the values for the slopes m_1 , m_2 , and m_3 , as given in figures 2, 3, and 4, respectively: For transition data, $\frac{0.902_5}{1.66_9} = 0.541$ (calc.) versus 0.533 (expt.). For fusion data, $\frac{0.342_3}{0.67_1} = 0.510$ (calc.) versus 0.533 (expt.).

The internal consistency calculations give deviations between the experimentally determined slope, m_3 , and the calculated one, m_2/m_1 , of +1.5 percent, for the transition data and -4 percent for the fusion data. The average of the two calculated slopes agrees to better than 1.5 percent with the experimentally determined one.

5.4. Conclusion

Consideration of the three criteria, namely, standard deviation of the slopes, internal consistency, and accuracy, as determined with the binary mixtures of standards, indicate an overall uncertainty of about 5 percent.

Averaging the results for the heats of transformation of Bi_2O_3 obtained from the mixtures with K_2SO_4 and Ag, yields:

$$L_{tr}\text{Bi}_2\text{O}_3(M \rightarrow c) = 9.9 \pm 0.5 \text{ kcal/mole}$$

$$L_f\text{Bi}_2\text{O}_3(c \rightarrow l) = 3.9 \pm 0.2 \text{ kcal/mole}$$

The sum of the entropy of transition and of fusion equals $\left(\frac{9900}{1003} + \frac{3900}{1098}\right) / 5 = 2.7 \text{ cal/}^\circ\text{K/g atom}$, a reasonable value [3].

6. Summary

To avoid problems inherent in a separate heat of reaction calibration of DTA equipment, a technique was developed which makes use of internal standards.

Binary mixtures of Bi_2O_3 and two standards, K_2SO_4 and Ag, were formulated in three weight ratios and subjected to three cyclic heat treatments, in the DTA equipment. Small amounts of mixtures, 0.2 to 0.4 g in total weight, were heated in platinum tubes which were isolated from the tubes containing the reference material, Al_2O_3 . Thermocouples, Pt-90 percent Pt:10 percent Rh, of fine wire were welded to the outside of the tubes. The modification of the sample holder and overall sensitivity of the equipment was found to respond to heat effects equivalent to 0.007 cal per mm^2 of the area under the peak.

A number of criteria were employed to check on possible reaction between Bi_2O_3 and the standards and to eliminate erroneous data. These criteria were as follows: Comparison of corresponding transformation ratios in successive heat cycles; comparison of the transformation ratio ($M \rightarrow c/c \rightarrow l$) in the Bi_2O_3 phase of mixtures with that in pure Bi_2O_3 ; x-ray powder analysis of mixtures at the completion of a determination; and, finally, observing the adherence of the data to linearity as prescribed by theory.

Except for the high weight ratio of Bi_2O_3 to K_2SO_4 in the 3.46:1 mixture, plots of ratios of transformation areas versus corresponding weight ratios were linear and passed through the origin. The presence of Ag in the Bi_2O_3 :Ag and the K_2SO_4 :Ag mixtures contributed to thermal transfer, and linearity was observed for all the weight ratios.

The data were analyzed according to (1) standard deviation of the slopes, (2) internal consistency, which is independent of the heat of transformation of the standards, and (3) agreement between calculated and selected literature value when one standard is mixed with the other. The heat of transition of Bi_2O_3 was found to be $9.9 \pm 0.5 \text{ kcal/mole}$ and the heat of fusion, $3.9 \pm 0.2 \text{ kcal/mole}$. The uncertainties are estimated limits of error, based on internal consistency and on the values of the standards.

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7. References

- [1] L. Belladen, Il sistema Bi_2O_3 -PbO (The System Bi_2O_3 -PbO), Gazz. chim. ital. **52**, II, 160-164 (1922).
- [2] K. K. Kelley, Contributions to Data on Theoretical Metallurgy: V, Heats of Fusion of Inorganic Substances, U.S. Bur. Mines Bull., No. 393, 166 pp. (1936); p. 26; Ceram. Abstr. **16** [5] 162 (1937).
- [3] O. Kubaschewski and E. LL. Evans, Metallurgical Thermochemistry, 426 pp, 3d ed., rev. (Pergamon Press, New York, 1958).
- [4] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffee, Selected Values of Chemical Thermodynamic Properties, NBS Cir. 500, (1952) 1268 pp.
- [5] E. M. Levin and C. L. McDaniel, The System Bi_2O_3 - B_2O_3 , J. Am. Ceram. Soc. **45** [8] 355-360 (1962).
- [6] G. Gattow and H. Schröder, "Über Wismutoxide, III, Die Kristallstruktur der Hochtemperaturmodifikation von Wismut (III)-oxid (δ - Bi_2O_3)", Z. anorg. allg. Chem. **318** [3-4] 176-189 (1962).
- [7] G. Gattow and D. Schütze, Über Wismutoxide, VI, Über ein Wismut (III)-oxid mit höherem Sauerstoffgehalt (β -Modifikation), Z. anorg. allg. Chem. **328**, [1-2] 45-67 (1964).
- [8] E. M. Levin and R. S. Roth, Polymorphism of bismuth sesquioxide. II. Effect of oxide additions on the polymorphism of Bi_2O_3 , J. Res. NBS **68A** (Phys. and Chem) No. 2, 197-206 (1964).
- [9] W. J. Smothers and Yao Chiang, Differential Thermal Analysis: Theory and Practice, 444 pp (Chemical Publ. Co., Inc., New York, 1958).
- [10] F. C. Kracek, The polymorphism of potassium nitrate, J. Phys. Chem. **34**, 225-47 (1930).
- [11] Isaac Barshad, Temperature and heat of reaction calibration of the differential thermal analysis apparatus, Am. Mineral. **37** [7&8] 667-694 (1952).
- [12] K. K. Kelley, Contributions to the Data on Theoretical Metallurgy. XIII. High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for the Elements and Inorganic Compounds, U.S. Bur. Mines Bull. 584, 1960. 232 pp.
- [13] (a) Cavallaro, Atti Real. Acad. Ital., Rend. Class Sci., Fiz., Mat. et Nat. [4-5] 520-526 (1934). (b) F. E. Wittig, Z. Elektrochem. **54**, 288 (1950). (c) W. Oelson, Arch. Eisenhüttenw. **28**, 1-6 (1957).
- [14] Ernest M. Levin and Robert S. Roth, Polymorphism of bismuth sesquioxide. I. Pure Bi_2O_3 , J. Res. NBS **68A** (Phys. and Chem.) No. 2, 189-195 (1964).
- [15] C. J. Penther, S. T. Abrams, and F. H. Stross, Semi-automatic Thermal Analysis Apparatus, Anal. Chem. **23**, 1459-66 (1951).

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